Atmospheric corrosion of stainless steel 07Cr18Ni10

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Abstract
In frame of UN ECE ICP programme two one-year exposure periods for stainless steel 07Cr18Ni10 (1.4301, AISI 304) were performed on network of European atmospheric test sites. The paper presents results of visual evaluation and corrosion mass losses of these panels. The data are compared with newly proposed standard for visual rating of corrosion of stainless steel.

Keywords stainless steel, atmospheric corrosion, corrosivity, mass loss, pitting corrosion

Introduction

The stainless steels (SS) had been developed in the beginning of 20st century and since this time there were applied in many industrial applications. Austenitic stainless steel has numerous technical applications because of its good mechanical properties and corrosion resistance. This resistance is the result of a very thin protective oxide film on the surface of the material, usually referred to as the 'air-formed passive film' formed by chromium oxide. However, corrosion does occur and is often localised a result of local breakdown of this film, e.g. pitting corrosion caused by deposition of contamination or high roughness of surface, etc.. Basically, the smoother the surface finish the better the corrosion resistance will be, since a rough surface will retain contaminants, such as chloride or ferrous ions, which in turn causes pitting and surface rust to form, commonly known as "tea staining" (Figure 1). But all these stains with corrosion product layer form the iniciation point for pitting corrosion.

Figure 1: "Tea staining" of stainless steel

Stainless steel was applied mainly in non-structural applications or in those applications where the structural properties of the component are not of primary importance, such as roofing, continuous façades, railings, and handrails are typical examples in which the resistance to corrosion and the inalterability of the aesthetic aspect are the premium factors. The first use if SS in atmospheric conditions – in architecture is the word known Chrysler building, New Your, USA erected in 1930. The cladding material was 18/8 stainless steel. After 65 years of exposure some dents and cracks were observed and superficial pitting near

an incinerator vent was detected [1, 2]. Because of its appearance, strength and high corrosion resistance, stainless steel is finding increasingly wide use in architecture for both exterior and interior applications. Most structural applications use austenitic grades 1.4301, 1.4401 or their low carbon variants 1.4307 and 1.4404. But the situation is slowly changed and stainless steel are now used also for structural applications as bridges and supporting collums, etc.. The sections used in construction and architectural applications might be typically 10 – 20 mm thick for structural members whilst lighter sections, as used for cladding, lintels etc, might be as thin as 1 – 3 mm.

Over the years many tests have been carried out with regard to environmental conditions and their effects on stainless steels. There are some data about corrosion mass loss and pitting corrosion of this type of stainless steel, mainly from marine or heavy industrial localities, and most of them for long-term corrosion exposure [3 - 6]. The conclusions from long-term atmospheric tests are that:

- the greatest degree of pitting corrosion occurred in heavy industrial atmospheres, with a high concentration of pollution, and marine environments;

- the rate and degree of corrosion of 316 stainless steel was substantially less than that of 304;

- the most corrosion occurs during the first years of exposure – Figure 2.

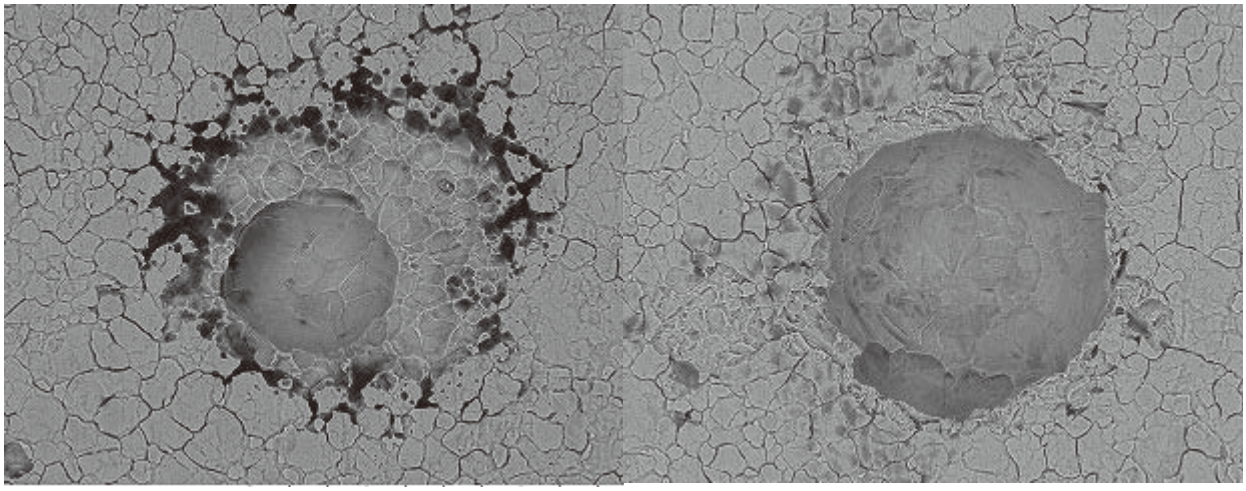

Figure 2: Pits formed on stainless steel 07Cr18Ni10 after 1 and 5 years of exposure, test site Okinawa, Japan [4]

Test exposure program

Panels of stainless steel 07Cr18Ni10 (according to EN 10088-1 with C < 0.07 %, 17.0 – 19.5 % Cr, 8 – 10.5 % Ni) of 150x100x1.5 mm were used. Panels were exposed on racks at 45° from the horizontal and were orientated south allowing a maximum exposure. For each exposure periods (2014-15 and 2017-18) there were used triplicate panels.

For this programme there were selected some atmospheric test sites from UN ECE ICP programme which represent urban and/or marine localities [7].

Figure 2: Example of exposure of panels – test site Vienna

Results of exposure

During whole exposure periods the basic climatic and pollution data were measured – Table 1 [7]. The air pollution by SO_2 is relatively low on test sites, the highest values were measured on test sites Kopisty, Bottrop, Svanvik and Katowice (ca 10 $\mu g.m^{-3}$). Chloride deposition was measured only on test sites Prague and Kopisty according to ISO EN 9225 by wet candle and modified dry plate, too. The long-term average values are 2.5 – 3.0 $mg.m^{-2}.d^{-1}$, i.e. background levels according to ISO EN 9223. Data for period 2017-18 are not available yet, but this exposure period was more warm with low precipitation on all test sites.

Table 1 – Survey of environmental parameters in period 2014-15 (yearly average values)

test site	T (°C)	RH (%)	SO_2 ($\mu g.m^{-3}$)	PM10($\mu g.m^{-3}$)
Prague, CZ - urban	11.0	72.5	4.6	6.0
Kopisty, CZ - industrial	10.8	71.4	11.4	11.1
Bottrop, DE - industrial	11.4	77.9	8.8	12.3
Rome, IT - urban	18.0	66.2	0.8	22.3
Cassacia, IT - urban, marine	15.5	73.4	1.2	22.8
Birkenes, NO - industrial	6.5	82.3	0.2	6.3
Berlin, DE – urban, highway	10.3	76.9	2.3	43.5
Svanvik, NO - industrial	1.5	76.3	7.4	3.5
Katowice, PL - industrial	10.7	71.4	13.4	21.3
Athens, GR - urban, marine	18.7	62.4	7.9	98.3
Vienna, AU - urban	12.0	70.5	4.2	11.8

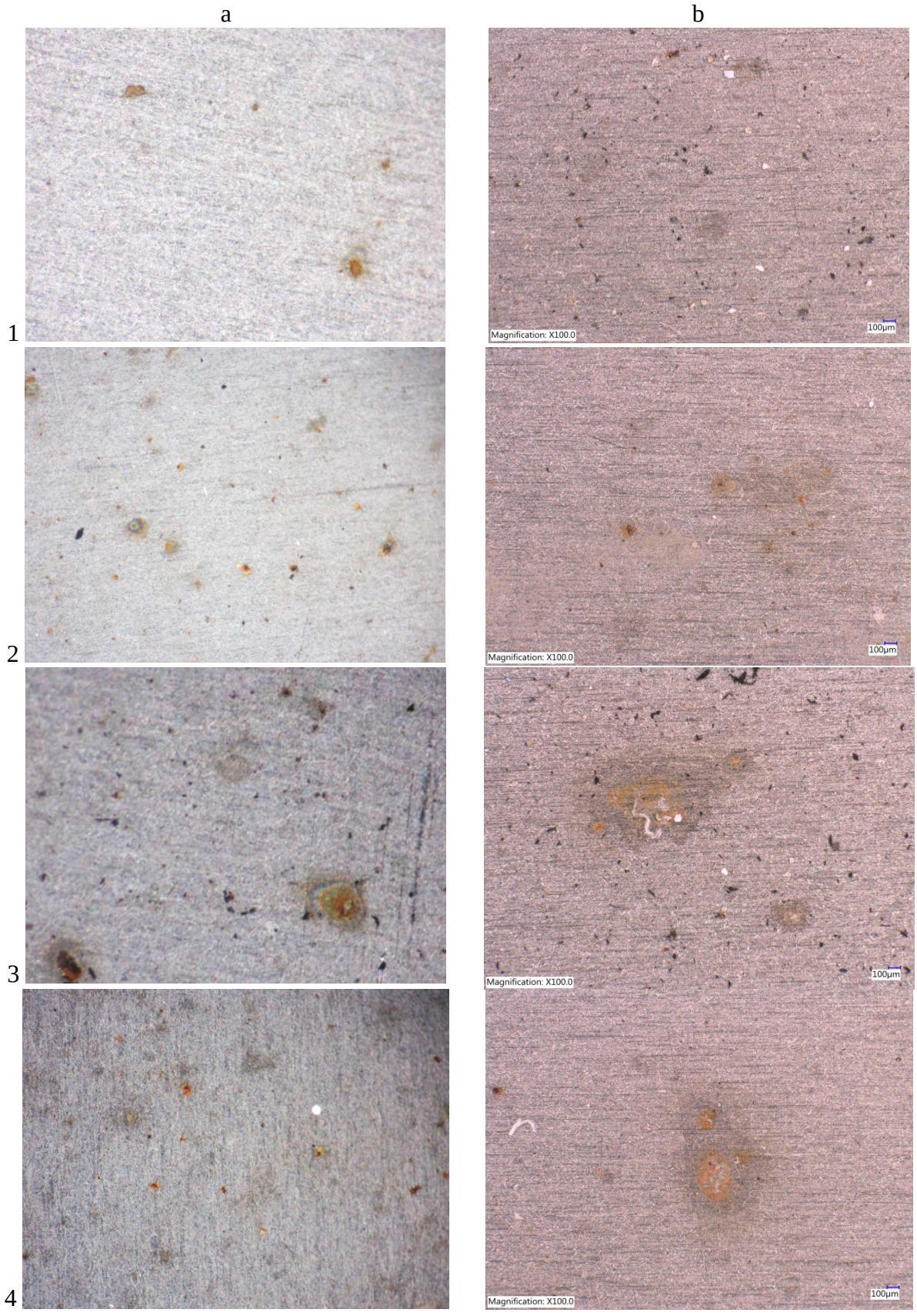

Figure 3: Details of surface of exposed panels in period 2014-15 (a) and 2017-18 (b) for test sites Bottrop (1), Rome (2), Berlin (3) and Athens (4)

Appearance of coupons

In appearance, all panels showed staining and discolouration after exposure. On test sites with high corrosion mass loss (Table 2) the high deposition of particles is evident – Figure 3. But even on panels on which practically any mass loss was estimated the small points of rainbow colours are evident to indicate breaking of passive chromium oxide layer – Figure 4.

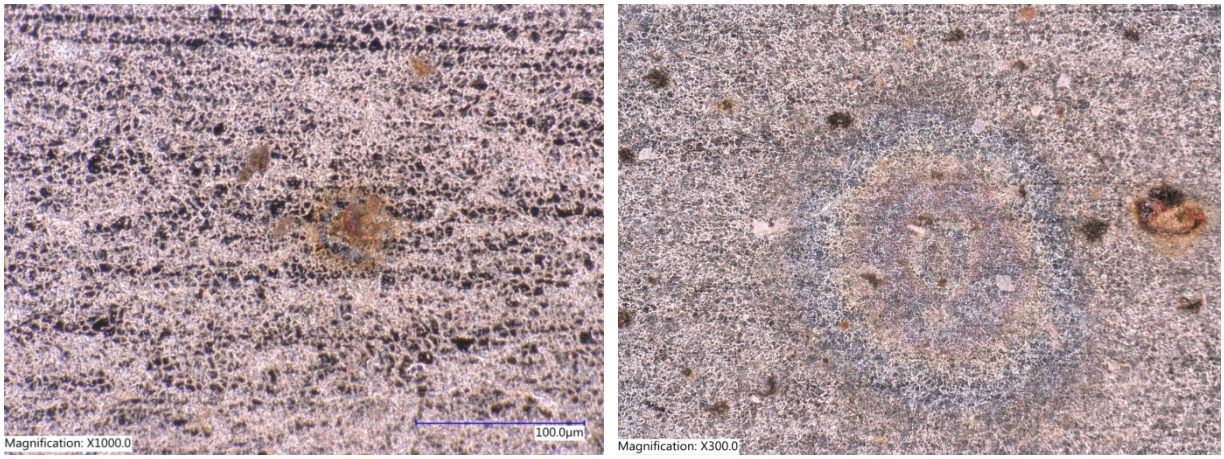

Figure 4: Examples of breaking of passive layer

Table 2 – Corrosion mass loss

test site	period 2014-15		period 2017-18	
	($g.m^{-2}$)	(µm)	($g.m^{-2}$)	(µm)
Prague, CZ - urban	0.0333	0.0042	0.0033	0.0004
Kopisty, CZ - industrial	0.0282	0.0036	0.0067	0.0008
Bottrop, DE - industrial	0.0503	0.0064	0.0222	0.0028
Rome, IT - urban	0.0467	0.0059	0.0144	0.0018
Cassacia, IT – urban, marine	0.0161	0.0020	0.0244	0.0031
Milano, IT - urban	-	-	0.0178	0.0023
Birkenes, NO - industrial	0.0380	0.0048	0.0200	0.0025
Paris, FR - urban	-	-	0.0189	0.0024
Berlin, DE – urban, highway	0.0970	0.0123	0.0222	0.0028
Svanvik, NO -	0.0278	0.0035	0.0122	0.0016
Katowice, PL - industrial	0.0300	0.0038	0.0100	0.0013
Athens, GR – urban, marine	0.0447	0.0057	0.0133	0.0017
Vienna, AU - urban	0.0333	0.0042	0.0111	0.0014
Zilina, SR - industrial	-	-	0.0322	0.0041
Split, C - urban, marine	-	-	0.0111	0.0014
Zagreb – urban	-	-	0.0011	0.0001

Corrosion mass loss of panels

Corrosion rates were determined by loss of weight, i.e. after removal of the surface corrosion products the overall mass loss of each panel can be determined. Thus, corrosion products were removed chemically following the ISO 8407. The results are given in Table 2.

The differentiation between corrosion mass loss on the same test sites at each exposure periods are caused mainly due to various climate conditions – these two periods differ mainly in temperatures and amount of precipitation.

Pitting corrosion

Surface morphology of panels with corrosion products were evaluated by 3D digital microscope Keyence VHX 5000 (Figure 4). The pitting corrosion had been found on some panels – Table 3. These tests sites represent localities with effect of chloride deposition (marine, de-icing salts) or with industrial pollution (Zilina). Pits can grow with an initial shallow dish, which may propagate via "earring" or small satellite pits. The size and morphology were seen to vary with exposure humidity, chloride deposition density and distance from the droplet edge.

Table 3 – Characteristics of pitting corrosion

test site	pits´ diameter (μm)	pits´ depth (μm)
Cassacia	20	2
Berlin	20	2
Athens	60	5
Zilina	60	3
Split	20	5

Discussion of results

The initial corrosion rate stainless steel 07Cr18Ni10 is very low and increase rapidly with increase in time with the formation of pits. One of reason of this exposure programme was to found some data for corrosivity classification for stainless steel. There was not estimated any relation between corrosion loss of carbon and stainless steel panels exposed at these two periods. As the climate conditions are different at each exposure period the correlation between them and very low corrosion mass loss is difficult.

The range of corrosion mass loss obtained in this exposure programme is not large enough for definition of corrosivity classification. The survey of published corrosion mass losses may give some database but in many cases these corrosion data are not completed with environmental data. In Table 4 there is the first proposal of classification system for atmospheric corrosion of stainless steel 07Cr18Ni10. This classification is based on uniform corrosion loss. But it is necessary to notice that the pitting corrosion is a better indicator of potential damage for stainless steel, but this characteristic evaluated after the first year of exposure is not available for representative number of exposed panels.

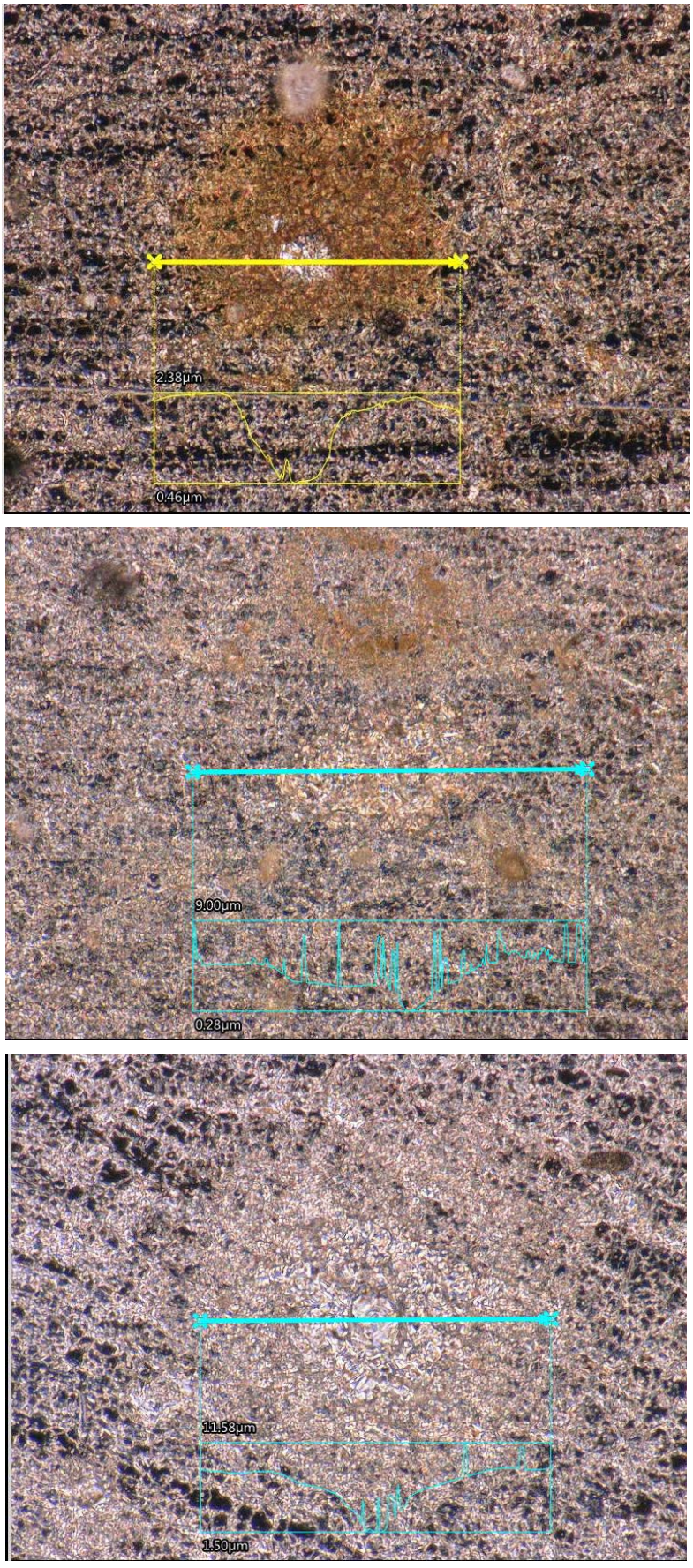

Figure 4: Examples of pitting corrosion of panels (Berlin, Athens, Split)

Table 4 – Proposal of corrosivity classification for stainless steel 07Cr18Ni10

category	mass loss ($g.m^{-2}$)	corrosion loss (μm)
C1	≤ 0.0200	≤ 0.0025
C2	≥ 0.0200 - 0.4000	≥ 0.0025 - 0.5000
C3	≥ 0.4000 - 0.8000	≥ 0.0500 - 0.1000
C4	≥ 0.8000 - 4.0000	≥ 0.1000 - 0.5000
C5	≥ 4.0000 - 7.5000	≥ 0.5000 - 1.000
CX	≥ 7.5000	≥ 1.0000

According to EN 1993-1-4 for stainless steels, life expectancy is not determined by subsequent protective treatments, but by the initial selection of materials, the design process and the fabrication procedures, and by their suitability for the environmental conditions. Although stainless steels can be subject to discolouration and staining, they are extremely durable in buildings. In aggressive industrial and marine environments, tests have shown no indication of reduction in component resistance even where a small amount of weight loss had occurred. However, unsightly rust staining on external surfaces might still be regarded as a failure by the user. Experience indicates that any serious corrosion problem is most likely to show up in the first two or three years of service. Table A.1 in this standard gives some very general recommendation for usage of stainless steel grades – stainless steel 07Cr18Ni10 is recommended for rural and urban environments, in industrial and marine environments it is recommended for "low" environments (i.e. least corrosive conditions for that type of environment). Such information is not the sufficient for evaluation of corrosion behaviour of stainless steel in atmospheric environments.

International (Eurocode 3, EN 1993-1-4) and national standards and guidelines (such as the German technical approval DIBt Z.30.3-6) work with a special scoring system when evaluating the suitability of certain stainless steel grades. This system takes the risks presented by the main influencing factors into account, from which a corrosion resistance factor (CRF) is calculated. Each risk factor (chlorides, SO_2, washing effect) is linked to a certain number of points. The CRF depends on the severity of the environment and is calculated as follows:

$$CRF = F1 + F2 + F3$$

where

F1 = risk of exposure to chlorides from salt water or de-icing salts (categories ranging from +1 to -15, mainly determined by the distance from the coast or roads, where de-icing salts are used)

F2 = risk of exposure to SO_2; (categories ranging from 0 to -15, determined by the average SO_2)

F3 = cleaning regime or exposure to washing by rain (categories ranging from +1 to -7).

Summing up all of the factors results in a number of points (the CRF) which then relate to five corrosion resistance classes – stainless steel 07Cr18Ni10 belongs to class II.

In ISO/TC 156/WG 4 there is proposed new standard *Rating method of rust and stains of atmospheric corrosion for stainless steels*. Rust and stains on stainless steels formed by atmospheric corrosion shall be rated by using ten photographic standards, in which the total area of rust and stains changes in the range of 0 to 100%. RN 0 corresponds to the total area of rust and stains almost 100% and RN 9 corresponds to the total area of rust and stains 0.01% or less. In proposed standard there are difficult to divide between RN 10 till RN 8. Example of rating scale for exposed panels is shown on Figure 5 in comparison to mass loss of them. The visual method cannot be used for determination of corrosion attack because each stain maybe iniciate pitting corrosion which progresion depends on exposure time and conditions.

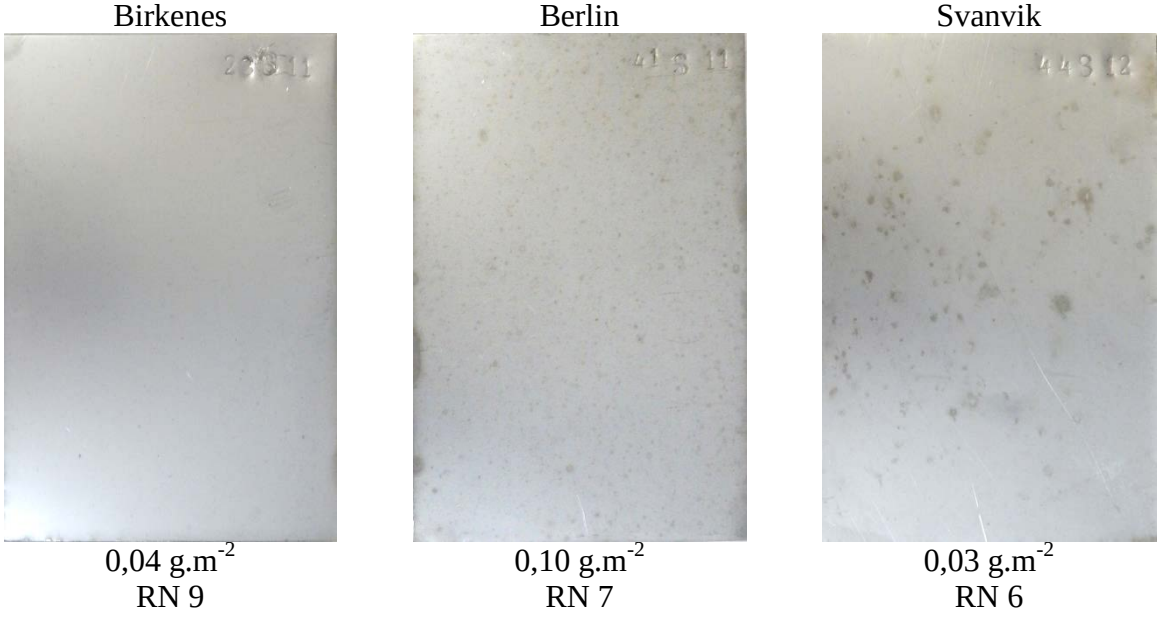

Figure 5: Examples of visual evaluation according proposed standard

Conclusion

The use of stainless steel has steadily increased over the past two decades. New stainless steel applications have appeared in sectors that were formerly the preserve of other steels or other materials. In architectural applications, aesthetic and performance requirements must be balanced against budget consideration for cost effective material specification. Materials selection decisions for architecture objects and other similar structures are often based on personal experience and budget limitations rather than scientific data. Usually the result is satisfactory, but when the wrong metal is used and problems arise, reputations can be damaged and remedial costs can be high. Predicting a metal's performance in exterior applications requires knowledge of the factors influencing corrosion. Unfortunately, good comparative corrosion data for stainless steels can be difficult to obtain.

The evaluation of corrosion of stainless steels from an aesthetic point of view has become important because even a small weight lost can cause a significant loss of appearance or aesthetic degradation [8, 9]. Aesthetic point of view may negatively affect the application of stainless steels, but the users sometimes do not identify the most critical mechanism of

corrosion attack of stainless steels – Figure 6. The crevice corrosion was considered as the dangerous, but the most critical was corrosion attack under washers combined crevice and pitting corrosion with 60 μm depth. So evaluation based only on visual evaluation is on sufficient and the corrosion experts need to be invited in this process.

Figure 6: Example of one highway infrastructure made from stainless steel 07Cr18Ni10 after 3 years of exposure

The corrosion loss and the pitting depth are important factors for selecting the materials, deciding the plate thickness, and estimating the lifetime. The aesthetic appearance is also important for stainless steels used for the exterior parts. The classification of corrosion losses and method for evaluating the appearance of stainless steels under atmospheric exposure has been required. Long-term exposures of stainless steels to natural atmospheric conditions show a bounding value for the pit size [10, 11].

Acknowledgements

This paper was prepared in frame of project MPO IP 8/2018 *Institutional support for long-term conception development of research organisation*. The authors also thanks to all participants of ECE UN ICP programme.

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